

Patent
Atty. Dkt. No. LYNN/0119

IN THE SPECIFICATION:

Please replace the paragraph beginning on page 3, line 28 with the following amended paragraph:

To be suitable for use in a ^{82}Rb generator, an ion exchange material must exhibit a high affinity for strontium but a low affinity for rubidium, allowing the ^{82}Rb daughter to be eluted from a column containing immobilized ^{82}Sr . Generators have been proposed that were based on a number of separation media including ~~Chelex-100~~ CHELEX 100 ion exchange material, Al_2O_3 , Sb(V) hexacyanoferrate, polyantimonic acid, titanium vanadate and hydrated tin(IV) oxide, with the hydrated tin(IV) oxide being the most widely used.

Please replace the paragraph beginning on page 5, line 30 with the following amended paragraph:

Sodium nonatitanate, $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$, is an inorganic ion exchange material that has been used for the removal of ^{90}Sr from neutral and alkaline nuclear wastes. The sodium nonatitanate of the present invention has a number of advantages over conventional organic ion exchange resins (e.g., ~~Chelex-100~~ CHELEX 100 ion exchange material) that include: very high selectivity for trace levels of strontium in the presence of molar concentrations of other ions at alkaline pH; very low affinity for rubidium; excellent radiation, chemical and thermal stability so that there is no release of contaminants (e.g. Ti) into the ^{82}Rb product; rapid reaction kinetics; high cation exchange capacity; absorbed ions readily stripped by treatment with dilute mineral acid allowing the sodium nonatitanate to be recycled, if desired; scale up of similar synthesis has already been demonstrated; and the sodium nonatitanate powder can be manufactured into pellets appropriate for column operations. Other chemically related sodium titanate materials suitable for use in the same manner as the aforementioned sodium nonatitanate ($\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$) include other titanate materials exhibiting high Sr affinity and low Rb affinity, including Sr-Treat (available from Selion Oy) and monosodium

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titanate (available from Boulder Scientific) It is also anticipated that analogous zirconates may exhibit similar properties.

Please replace the paragraph beginning on page 7, line 17 with the following amended paragraph:

These Examples investigated the suitability of sodium nonatitanate for the use in separating ^{82}Sr from irradiated targets and in the construction of a $^{82}\text{Sr}/^{82}\text{Rb}$ generator. Initial batch experiments compared the rubidium and strontium selectivities of a number of different sodium nonatitanate samples with commercially available ion exchange materials (e.g. AW 500 ion exchange material, Chelex-400 CHELEX 100 ion exchange material) and some experimental materials that had also exhibited high strontium selectivities (e.g. sodium titanasilicate). Column experiments were then performed using target simulants and generator simulants on materials that exhibited favorable selectivity characteristics. Some work was also performed to investigate the likely interference from other isotopes present in irradiated targets on the production of ^{82}Sr .

Please replace the table beginning on page 8, line 27 with the following amended table:

Table 1. Characteristics of ion exchange materials evaluated in this study.

Material	Source	Sample Preparation
Na-Clinoptilolite	GSA Resources, AZ	Ground to powder.
AW500	Aldrich (1.6 mm Pellets)	Ground to powder.
Hydrous SnO_2	Synthesized in house	$\text{NaOH} + \text{SnCl}_4$. Washed with acetic acid/sodium acetate buffer.
K ⁺ Pharmacosiderite ($\text{K}_3\text{H}(\text{TiO})_4(\text{SiO}_4)_3 \cdot 4\text{H}_2\text{O}$)	Synthesized according to literature method.	None. Used as synthesized.
Sodium Titanosilicate ($\text{Na}_2\text{Ti}_2\text{O}_3\text{SiO}_4 \cdot 2\text{H}_2\text{O}$)	Synthesized according to literature method.	None. Used as synthesized.

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AG 50W-X8 (Na+) <u>ion exchange material</u> (25 - 50 Mesh)	BioRad. Strong acid ion exchange resin.	Converted to Na+ form (for alkaline solutions only)
Chelex-100 (Na+) <u>CHELEX 100 ion</u> <u>exchange Material (Na+)</u> (50 - 100 Mesh)	BioRad. Chelating resin with iminodiacetic acid functionality.	None. Used as received.
Sodium Nonatitanate	Honeywell, IL	None. Used as received.
Hydrous SiO ₂	Synthesized in house	Acetic acid hydrolysis of tetraethyl orthosilicate. Washed with H ₂ O
Hydrous TiO ₂	Synthesized in house	Hydrolysis of titanium isopropoxide. Washed with H ₂ O
Hydrous ZrO ₂	Synthesized in house	ZrOCl ₂ + NaOH. Washed with deionized water.

Please replace the table beginning on page 10, line 11 with the following amended table:

Table 2. Strontium selectivity data from unbuffered sodium chloride solutions.

Ion Exchange Material	K _d mL/g			
	1M NaCl	0.1M NaCl	0.01M NaCl	0.001M NaCl
Na-Clinoptilolite	8	124	3,260	36,900
AW500	1,860	88,300	1,270,000	1,210,000
Hydrous SnO ₂	767	43,000	124,000	51,800
K+ Pharmacosiderite	18,300	251,000	594,000	281,000
Sodium Titanosilicate	556,000	273,000	119,000	42,900
AG 50W (Na+)	32	3,380	365,000	2,510,000
Chelex-100 (Na+) <u>CHELEX 100 ion</u> <u>exchange material (Na+)</u>	610	26,400	726,000	1,300,000
NaTi (Honeywell)	80,600	1,030,000	258,000	166,000
NaTi (No hydrothermal)	1,530,000	2,570,000	739,000	372,000
NaTi (170°C, 21hr)	1,030,000	1,240,000	272,000	172,000
NaTi (170°C, 3d)	959,000	633,000	218,000	93,100

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NaTi (170°C, 7d)	167,000	834,000	264,000	90,400
NaTi (200°C, 21hr)	439,000	1,390,000	197,000	120,000
NaTi (200°C, 3 d)	261,000	898,000	251,000	158,000
NaTi (200°C, 7d)	195,000	955,000	265,000	214,000
ZrO ₂	3,360	52,200	213,000	232,000

Please replace the table beginning on page 10, line 33 with the following amended table:

Table 3. Strontium selectivity data from unbuffered rubidium chloride solutions

Material	K _d mL/g 1M RbCl	0.1M RbCl	0.01M RbCl	0.001M RbCl
Na-Clinoptilolite	19	3	88	11,000
AW500	9,750	107,000	1,020,000	1,280,000
Hydrous SnO ₂	766	66,100	104,000	51,800
K ⁺ Pharmacosiderite	1,950	40,800	419,000	427,000
Sodium Titanosilicate	12,600	94,700	164,000	179,000
AG-50W (Na ⁺)	44	3,870	237,000	800,000
<u>Chelex-100 (Na⁺)</u>				
<u>CHELEX 100 ion</u>				
<u>exchange material (Na⁺)</u>	1,580	38,400	555,000	977,000
NaTi (Honeywell)	13,900	108,000	279,000	324,000
NaTi (No hydrothermal)	14,220	116,000	345,000	429,000
NaTi (170°C, 21hr)	10,500	71,700	193,000	205,000
NaTi (170°C, 3d)	15,100	39,500	68,000	95,200
NaTi (170°C, 7d)	23,000	53,800	31,200	110,000
NaTi (200°C, 21hr)	11,000	66,400	110,000	103,000
NaTi (200°C, 3 d)	10,600	56,800	146,000	158,000
NaTi (200°C, 7d)	10,500	57,400	146,000	158,000
ZrO ₂	3,000	42,400	184,000	221,000

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Please replace the table beginning on page 12, line 7 with the following amended table:

Table 4. Rubidium selectivity data from unbuffered sodium chloride solutions.

Material	86Rb K_d mL/g			
	1M NaCl	0.1M NaCl	0.01M NaCl	0.001M NaCl
AW500	116	620	4,920	21,900
Hydrous SnO ₂	1	6	36	290
K ⁺ Pharmacosiderite	148	475	2,030	4,020
Sodium Titanosilicate	8,010	194,000	114,000	75,800
AG 50W (Na ⁺)	7	75	688	6,680
Chelex 100 (Na⁺)				
<u>CHELEX 100 ion</u>				
<u>exchange material (Na⁺)</u>	3	8	43	256
NaTi (Honeywell)	9	102	488	817
NaTi (No hydrothermal)	4	59	280	446
NaTi (170°C, 21hr)	9	56	209	297
NaTi (170°C, 3d)	7	46	198	311
NaTi (170°C, 7d)	3	15	47	71
NaTi (200°C, 21hr)	8	79	334	502
NaTi (200°C, 3d)	8	52	207	307
NaTi (200°C, 7d)	4	25	111	178
ZrO ₂	1	12	60	154

Please replace the paragraph beginning on page 13, line 1 with the following amended paragraph:

Hydrous tin dioxide exhibited some of the lowest rubidium affinities and was comparable with ~~Chelex 100~~ CHELEX 100 ion exchange material, the best of the nonatitanates and the hydrous zirconium dioxide. However, hydrous tin dioxide exhibited much lower strontium K_d values than the nonatitanates. Therefore, nonatitanate materials are preferred because they have higher strontium/rubidium separation factors. Hydrous tin dioxide also has a limited pH stability range and significant dissolution and release of absorbed strontium is likely to occur should any significant pH perturbations occur outside the range of pH 4 to pH 9. Radiation stability of hydrous tin dioxide is also limited, with particle breakdown causing current 82-Rb generators to be replaced before decay

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has reduced the 82-Rb below useable levels.

Please replace the paragraph beginning on page 15, line 4 with the following amended paragraph:

Figure 1 clearly shows the exceptionally high affinity of the sodium nonatitanate materials in comparison with the currently utilized organic resin ~~Chelex-100~~ CHELEX 100 ion exchange material. All of the sodium nonatitanates performed equally well in the buffered rubidium target solutions indicating that the synthetic conditions are not too important when the material is being used in solutions containing high concentrations of rubidium ions. Thus, by replacing the ~~Chelex-100~~ CHELEX 100 ion exchange material with sodium nonatitanate, a more efficient 82Sr isolation can be achieved.

Please replace the table beginning on page 15, line 32 with the following amended table:

Table 5. Strontium and rubidium absorption from simulated molybdate target solutions

Material	Sr K _d mL/g	Rb K _d mL/g	Separation Factor
AW500	7,070	194	36.4
K+ Pharmacosiderite	187,000	142	1320
Sodium Titanosilicate	547,000	6500	84.2
Chelex-100 (Na+)			
<u>CHELEX 100 ion exchange material (Na+)</u>	3,120	5	624
AG 50W-X8 (Na+)			
<u>ion exchange material</u>	69	18	3.83
NaTi (Honeywell)	337,000	27	12,500
NaTi (No hydrothermal)	1,690,000	12	141,000
NaTi (170°C, 21hr)	1,000,000	12	83,300
NaTi (170°C, 3d)	829,000	14	59,200
NaTi (170°C, 7d)	324,000	3	108,000
NaTi (200°C, 21hr)	954,000	12	79,500
NaTi (200°C, 3 d)	687,000	11	62,500
NaTi (200°C, 7d)	772,000	9	85,800
ZrO ₂	168,000	8	21,000

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Please replace the paragraph beginning on page 16, line 17 with the following amended paragraph:

From this data, it is clear that the sodium nonatitanate materials are far superior to ~~Chelex~~ 400 CHELEX 100 ion exchange material and AG 50W-X8 ion exchange material resins for the recovery of ^{82}Sr from irradiated molybdenum targets. High K_d values in excess of 500,000 mL/g indicate that almost 100% strontium removal was achieved by some of the nonatitanate samples, with the residual strontium in solution approaching background levels. In the alkaline conditions used in this test, the ~~Chelex 400~~ CHELEX 100 ion exchange material resin had the lowest affinity for strontium of all of the materials evaluated. The selectivity of the sodium nonatitanate for rubidium was lowest for the sodium nonatitanate material that was prepared by heating for 1 week at 170°C to obtain a relatively crystalline product. However, strontium selectivity also decreased with increasing reaction time.

Please replace the paragraph beginning on page 17, line 3 with the following amended paragraph:

Sodium nonatitanate has a relatively low affinity for strontium at pH values less than 6, and was not expected to exhibit any affinity for strontium from the acidic molybdate target solutions prior to the addition of sodium hydroxide. K_d values were determined to confirm this and to compare it with the K_d values for both ~~Chelex 400~~ CHELEX 100 ion exchange material and AG 50W-X8 ion exchange material under identical conditions. The data obtained is shown below in Table 6.

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Please replace the table beginning on page 17, line 9 with the following amended table:

**Table 6. The affinity of selected ion exchange materials
for strontium in acidic molybdate target solutions**

Ion Exchange Material	Sr K _d mL/g	Final pH of Solution
Chelex-100		
<u>CHELEX 100 ion exchange material</u>	25	1.43
AG 50W-X8		
<u>ion exchange material</u>	18,300	1.42
Sodium Nonatitanate (Honeywell)	1,260 1.53	

Please replace the paragraph beginning on page 17, line 17 with the following amended paragraph:

These data clearly indicate that for the processing of acid molybdate solutions, the strong acid ion exchange resin AG 50W-X8 ion exchange material is the preferred medium. However, the Sr K_d value of 18,300 mL/g in the acidic media is nearly two orders of magnitude lower than the K_d value of 1,690,000 mL/g that was obtained for the best of the sodium nonatitanate materials in alkaline molybdate solutions. Consequently, it is evident that ⁸²Sr can be recovered more effectively from alkaline solution using sodium nonatitanate than is currently achieved using AG 50W-X8 ion exchange material from acidic media.

Please replace the paragraph beginning on page 17, line 26 with the following amended paragraph:

The processing of either rubidium chloride or rubidium metal targets follows a similar procedure once the target has been successfully dissolved. In essence, ⁸²Sr needs to be selectively extracted from a solution of RbCl in a 0.1 M NH₃ / 0.1M NH₄Cl buffer adjusted to a pH of between 9 and 10. Batch experiments were performed in simulated buffer solutions to determine the

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strontium selectivity in the presence of high concentrations of rubidium ions. Only the ion exchange materials that exhibited high strontium selectivities in the initial scoping studies with NaCl solutions were evaluated. K_d values were obtained as described previously. Two rubidium chloride solutions were selected which represent typical rubidium concentrations obtained during the processing of rubidium metal (1.95 M Rb+) and rubidium chloride targets (0.68 M Rb+). In both cases, ~~Chelex-100~~ CHELEX 100 ion exchange material is used in the preliminary step to remove the ^{82}Sr from the buffered rubidium solutions. The K_d values for the ion exchange materials are shown in Figure 1.

Please replace the paragraph beginning on page 18, line 3 with the following amended paragraph:

In the buffered rubidium solutions, there is little difference between the different nonatitanates evaluated. This is in stark contrast to the sodium molybdate solutions where a large variation in the performance of the titanates was observed. The nonatitanates were clearly the most effective materials at removing strontium from the buffered solutions with strontium K_d values of around 15,000 mL/g in 0.68 M Rb+ solutions and approximately 5,000 mL/g in 1.96 M Rb+ solutions. By contrast, ~~Chelex-100 ion exchange~~ CHELEX 100 ion exchange material resin gave K_d values of less than 1,000 mL/g in both solutions. Hydrous titanium oxide and hydrous tin oxide also exhibited appreciable K_d values, but they performed less efficiently than the nonatitanates in both solutions. Consequently, this data demonstrates that using sodium nonatitanate in place of ~~Chelex 100 ion exchange~~ CHELEX 100 ion exchange material resin will greatly increase the amount of strontium extracted from the target solutions.